

Computer Center

VIII-O Theoretical Studies on Electronic Structure and Dynamics of Electronically Excited States in Polyatomic Molecules

VIII-O-1 Theoretical Study of the Potential Energy Surfaces and Bound States of HCP

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Global, ab initio potential energy surfaces for HCP in its ground $1^1\Sigma^+$ ($1^1A'$) and low-lying excited $1^1A''$, $2^1A'$, and $1^1\Delta$ ($2^1A''$) electronic states are determined. The multireference configuration interaction method at the double zeta with polarization basis set level is used, although some calculations augmented with diffuse functions are also discussed. Numerous quantum mechanical rovibrational states are then obtained for these surfaces, with emphasis on those corresponding to excited electronic state levels which have not been studied theoretically before. The results agree reasonably well with available experimental data for the $1^1A''$ state. Furthermore, the presence of certain local minima on the $1^1A''$ and $2^1A'$ surfaces leads to one new series of levels on the $1^1A''$ surface, and two new series on the $2^1A'$ surface.

VIII-O-2 A Comparative Study of the Quantum Dynamics and Rate Constants of the $O(^3P) + HCl$ Reaction Described by Two Potential Surfaces

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Wave packet calculations, using direct and damped- L^2 real propagation methods, of initial state-resolved and cumulative reaction probabilities for the $O(^3P) + HCl$ ($1^1\Sigma^+$) $\rightarrow$ $OH(^2\Pi) + Cl(^2P)$ reaction are reported. Results are obtained using the recently developed "S4" potential surface of Ramahandran co-workers and, for comparison, the earlier, Koizumi, Schatz and Gordon (KSG) potential energy surface. Most calculations are for total angular momentum $J = 0$, although some $J > 0$ centrifugal sudden results are also obtained. The thermal rate constant and the rate constant for HCl ($v = 1$) are obtained from the $J = 0$ cumulative reaction probability and J -K-shifting, using standard transition-state rotation constants. This type of shifting is justified by examining limited centrifugal sudden calculations. The S4 surface is shown to yield some surprising results. For example, despite a significantly higher ground state adiabatic barrier than the KSG surface, the thermal rate constant is not significantly different from one obtained with the

KSG surface, although the one for the vibrationally excited HCl is.

VIII-O-3 Determination of the Global Potential Energy Surfaces for Polyatomic Systems

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Computational algorithm of the determination of the global potential energy surfaces for polyatomic systems are developed with using the interpolant moving least squares scheme, which was proposed by Ishida and Schatz [*Chem. Phys. Lett.* **314**, 369 (1999)]. In this scheme, any derivatives in quantum-chemical calculations are not required to construct the surface and in contrast with previously developed schemes based on Shepard interpolation alone. In our new algorithm, the molecular conformations are generated with the Monte Carlo sampling, and then the ab initio calculations for all of the conformations are performed by the parallel computing at the same time. Therefore, we have good advantage for computational time for the normal calculations. Application is made to the tetra-atomic systems, the $2OH \leftrightarrow H_2O + O$ reaction.

VIII-O-4 Semiclassical Study of Nonintegrable Systems

TAKAMI, Toshiya

We study nonadiabatic processes in classically nonintegrable systems such as 2D billiards and kicked rotators to reveal essence of the dynamical characters in highly excited states of molecules. Theoretical treatment of the nonadiabatic transition between adjacent levels through an avoided crossing was studied first in pioneering works by Landau, Zener, *etc.* In the nonintegrable systems, however, the Landau-Zener formula cannot be applied because those systems contain essentially many levels, *i.e.* nonadiabatic couplings between adiabatic states cannot be ignored everywhere.

On numerical experiments in nonintegrable systems, we found non-Landau-Zener behavior, and we pointed that the phenomenon arises from nonadiabatic couplings between eigenstates on the endpoints. In order to describe the extra-transition theoretically, we introduce "boundary expansion" to get higher order terms of the nonadiabatic couplings. By the use of the expansion, we construct a new base which can describe nonadiabatic transition locally even in nonintegrable systems. This base is shown to be the same as superadiabatic base by M.V. Berry.

VIII-O-5 Development of *ab initio* MD Method Based on the Direct Evaluation of CAS-SCF Energy Derivatives

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We have been developing an *ab initio* molecular dynamics program to investigate the reaction dynamics of large scale problems, *i.e.*, surface reactions, and biological systems. Since we employed parallelized version of McMurchie-Davidson's algorithm to evaluate both AO integrals and derivatives of AO integrals, the most time consuming step of electronic structure calculations has been carried out in a tractable way. At each time steps of MD calculations, we obtain analytical energy derivatives of complete active space (CAS) wavefunctions. We continue to develop the codes for non adiabatic and spin-orbit coupling matrix elements. Our direct method can easily extend to apply a number of interesting problems including non adiabatic reactions and spin forbidden processes. For the benchmark test purposes of this program system, the low-lying singlet and triplet surfaces of $\text{CH}^+ + \text{H}_2 \leftrightarrow \text{C} + \text{H}_3^+$ is investigated by using direct *ab initio* molecular dynamics.